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Invited Review Article

Molybdenum isotope variations in magmatic rocks

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ABSTRACT

The application of Mo isotopes to study geodynamic processes is a rather new development that has gained considerable momentum over the past few years. Its redox-sensitivity causes significant mass-dependent isotope variability in low-temperature environments – mainly during weathering, sediment deposition and seafloor alteration. Potentially, these fractionated Mo isotope characteristics of surface materials could be used to identify recycled crustal components in mantle sources. Here we provide an overview of the first studies on mass-dependent isotope variations of Mo in igneous rocks and the Mo isotopic characteristics of major geochemical reservoirs before assessing the potential of Mo isotope variations as a new tracer in mantle geochemistry.

Mass-dependent Mo isotope variations induced by magmatic differentiation are in general muted owing to the incompatibility of Mo in common igneous minerals. However, fractionation of Mo isotopes by hydrous silicate mineral phases has been suggested. Sulphide fractionation can potentially have a marked influence on the Mo isotope composition of evolving magmatic systems but does not appear to be a major influence due to the limited modal abundance of sulphide phases precipitated during differentiation. The largest Mo isotope variations in igneous systems reported so far are found in arc-related rocks. Currently available data suggest that the $\delta^{98/95}$Mo values (i.e. the ^{98}Mo/^{95}Mo ratio relative to the reference material NIST SRM 3134) measured in arc basalts are higher than those of the upper mantle. This offset appears to be linked to the addition of isotopically heavy slab-derived fluid to the arc melts, whereby heavier Mo isotopes become enriched in the fluid as a result of the slab-dehydration. In contrast, lighter $\delta^{98/95}$Mo compositions found in some arc-related lavas could be linked to geochemical tracers commonly associated with sediment melt contribution. Overall, mass balance considerations suggest that the recycled crustal material has a Mo isotope composition equal to or most likely lighter than that of fresh oceanic crust.

Chondritic meteorites display a remarkably homogeneous $\delta^{98/95}$Mo of -0.16 ± 0.02‰ suggesting a similar bulk composition for the inner solar system and thus the Earth. Residual Mo in the mantle after core formation is expected to be isotopically heavy but for temperatures in excess of 2500 K, typically proposed for core-mantle equilibration, the difference in $\delta^{98/95}$Mo of the mantle relative to chondrite is <0.1‰. Analyses of Mo isotopes in mid-ocean ridge basalts suggest a slightly sub-chondritic composition of the depleted mantle ($\delta^{98/95}$Mo $= -0.21 \pm 0.02$‰). Similarly, late Archean komatiites yield slightly sub-chondritic $\delta^{98/95}$Mo of ca. -0.21 ± 0.06‰ suggesting that the mantle may have maintained a similar Mo isotope composition throughout the post-Archean. The Mo isotope composition of the continental crust is currently the least well-constrained value of major geochemical reservoirs. A preliminary estimate available for maximum value for the upper continental crust yields a super-chondritic $\delta^{98/95}$Mo of ca. +0.15‰. The value of the bulk continental crust remains unknown but is likely to be lower. Assuming a chondritic bulk silicate Earth differentiates solely into continental crust and depleted mantle reservoirs, the $\delta^{98/95}$Mo of the average continental crust would range between +0.1 and +0.35‰. This is broadly compatible with the initial observations, making Mo the first non-radiogenic isotopic system to show such an apparent complementarity between the continents and mantle reservoirs. Given that deep recycled crust is characterised by $\delta^{98/95}$Mo lower than that of depleted mantle, subduction provides a mechanism by which to affect this change.

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1. Introduction

In the modern tectonic cycle, partial melting creates oceanic crust at mid-ocean ridges and continental crust at convergent margins and, as a consequence, gives rise to a melt-depleted mantle (Hofmann, 1988). Subduction returns oceanic crust and part of the continents into the mantle. Chemical geodynamics uses the contrasting compositions of the three major components in the system to trace its evolution, in particular the distinct radiogenic isotope compositions they develop with time (Allègre, 1982, Zindler and Hart, 1986). The continents record a long-term isolation of elements that are incompatible in the crystal structure of common mantle minerals and there is a complementary signature in the mantle (Armstrong, 1968; DePaolo and Wasserburg, 1976; O'Nions et al., 1979). While the continental crust is readily accessible, direct samples of the mantle are rare. Thus the composition of the mantle is most commonly studied through basalts that erupted on the ocean seafloor. These basalts represent partial melts of the underlying mantle that have escaped contamination by the continental crust and hence indirectly record mantle compositions.

Numerous isotope and trace element studies of oceanic basalts show that the residual mantle is far from homogeneously depleted (e.g. Gast et al., 1964; Tatsumoto et al., 1965; Hedge, 1966; Tatsumoto, 1966). Two lines of evidence suggest that its incompatible element inventory is continuously re-fertilised, due to the recycling of crustal materials, leading to pronounced chemical and isotopic heterogeneity. Firstly, portions of oceanic crust (ocean islands as well as some mid-ocean ridges) show geochemical signatures that cannot be explained as remnants of un-differentiated mantle (also called bulk silicate Earth) or its simple melt depletion (Roden et al., 1994). Rather, their composition suggests that besides a depleted mantle source they contain at least one enriched component that has experienced an isolated long-term chemical evolution (e.g. Hawkesworth et al., 1979). Secondly, subduction of oceanic and continental lithosphere along destructive plate margins directly shows the return of enriched components at least into the upper and possibly into the lower mantle.

The role of plate tectonics in shaping the composition of the mantle was recognised early (Armstrong, 1968), but the notion gained important traction in the 1980s (see Hofmann and White, 1982). In their simplest form, such conceptual models suggest that the enriched signatures sampled by some ocean island basalts represent recycled, crustal material (Chase, 1981; Hofmann and White, 1982). This crust is assumed to have been processed through ancient subduction zones and matured as isolated entities, before being incorporated into the mantle sources of the oceanic basalts. Since then, this basic model has been expanded as well as modified to reconcile it with an ever increasing number of geochemical data for oceanic basalts (e.g. Stracke et al., 2005) as well as our more refined understanding of geological processes that operate in destructive plate margins and within the mantle; such as the chemical and isotopic modification of crustal components during seafloor alteration and subduction (e.g. Hart and Staudigel, 1982; Chauvel et al., 1992); the role of subduction erosion (e.g. Willbold and Stracke, 2010) and delamination and foundering of continental lithosphere (e.g. McKenzie and O'Nions, 1983; Lustrino and Dallai, 2003) as well as mantle metasomatism as a process to generate enriched mantle signatures (e.g. Zindler et al., 1979; Niu and O'Hara, 2003; Donnelly et al., 2004; Pilet et al., 2005).

The degree to which all these processes contribute to the compositional evolution of the Earth's mantle is a matter of debate. Yet, with the possible exception of intra-mantle metasomatism, large-scale mass transfer between the key reservoirs appears to be the underlying cause of the re-enrichment of the mantle. Classically, long-lived radiogenic isotope data have been used to describe the framework of isotope heterogeneities in the mantle and to reconcile them with different components (e.g. Allègre, 1982; Zindler and Hart, 1986). While these data have, to this date, proven to be invaluable pillars in identifying as well as characterising enriched mantle components, the information contained in radiogenic isotope systems must first be converted into a geochemical fingerprint of a specific mantle component (i.e. its parent/daughter element ratio) before being able to identify its nature. This requires knowledge of the residence time of a recycled component within the mantle, which is – without exception – unknown.

The trace element composition of magmas has been extensively used to help place constraints on the origin of enriched components in the mantle (Jochum et al., 1983; Hofmann, 1986; Newsom et al., 1986; Weaver, 1991b). New analytical techniques allow increasingly more comprehensive sets of incompatible trace element data for oceanic basalts to be included in our models, providing a fuller characterisation of the origin of enriched mantle components (Donnelly et al., 2004; Workman et al., 2004; Willbold and Stracke, 2006). However, element concentrations in partial melts only indirectly reflect those of their mantle source (Schilling and Winchester, 1967; Gast, 1968; Shaw, 1970), but the effect of elemental fractionation during melting can be minimised by using ratios of highly-incompatible trace elements (e.g. Hofmann et al., 1986). Combined with radiogenic isotope data, this approach enabled a refinement in the characterisation of mantle heterogeneity and allowed the assessment of the validity of our existing models of mantle recycling (e.g. Sun and McDonough, 1989; Eisele et al., 2002; Niu et al., 2002; Stracke et al., 2003b; Donnelly et al., 2004; Willbold and Stracke, 2006). Yet, even highly incompatible trace element ratios in partial mantle melts are governed not only by the chemical, but also by the mineralogical composition of the source and thus also depend on exact conditions of the melting process (e.g. Stracke and Bourdon, 2009).

More recently, isotope variations (e.g. O, B, D/H, Li, Fe, Tl, Si, S, U and noble gasses) in oceanic basalts and mantle xenoliths have been used to identify and characterise mantle heterogeneities. (e.g. Chaussidon and Marty, 1995; Harmon and Hoefs, 1995; Gurenko and Chaussidon, 1997; Eiler et al., 2000; Kingsley et al., 2002; Elliott et al., 2006;

Holland and Ballentine, 2006; Nielsen et al., 2006; Sharp et al., 2007; Bonifacie et al., 2008; Shaw et al., 2012; Cabral et al., 2013; Labidi et al., 2013; Williams and Bizimis, 2014; Andersen et al., 2015; Pringle et al., 2016). Unlike radiogenic isotope variations, the information contained in these systems is independent of the residence time of the recycled components in the mantle but should be highly sensitive to their prior presence at the surface, where redox-dependent isotope fractionation should be greatest. Along these lines, Mo isotope variations in magmatic rocks have attracted considerable interest to study the origin of enriched mantle components. As a redox sensitive element during weathering, sediment transport and deposition, as well as biological cycling (Barling and Anbar, 2004; Tossell, 2005; Wasylenki et al., 2008; Nägler et al., 2011; Zerkle et al., 2011), Mo isotope data coupled with Mo concentrations have been used to reconstruct the history of the redox state of the oceans (Barling et al., 2001; Siebert et al., 2003; Anbar, 2004; Pearce et al., 2008; Gordon et al., 2009). In contrast to many previous mass-dependent isotope systems, Mo behaves as an incompatible and refractory element in magmatic systems. Its chemical properties result in significant changes in its charge and coordination during low- and high-temperature processes and thus make it an attractive potential tracer of crust-mantle recycling processes.

In this contribution, we review the current literature on Mo isotope data for magmatic systems and use this to explore the feasibility of using Mo isotopes in oceanic basalts as a tracer of recycled crustal material in the Earth's mantle. A major analytical challenge arises from the low concentrations of Mo in magmatic rocks and a series of new chemical separation techniques have been developed to cope with large sample sizes (Section 2). Beyond that, the effects of potential isotope fractionation during fractional crystallisation need to be characterised (Section 3) before the Mo isotope composition of samples from the oceanic and continental crust can be assessed and interpreted within their geological framework. In the context of crustal recycling at destructive plate margins, the geological processes that operate in subduction zones (i.e. dehydration reactions, sediment subduction, sediment melting) may alter the isotopic composition of the recycled crust (Section 4). A better understanding of these processes will enable us – within the limits of the current global data set of Mo isotopes for magmatic rocks – to rationalise the Mo isotope composition of the residual (depleted) mantle and the continental crust relative to bulk silicate Earth (Section 5). Overall, we can then use this framework to assess how Mo isotope variations in oceanic basalts can be used to trace enriched components in the Earth's mantle (Section 6).

2. Geochemistry of Mo and analytical methods

Molybdenum is a transition metal that has seven rather evenly distributed isotopes spread over a comparatively large mass range: ^{92}Mo (14.84%), ^{94}Mo (9.25%), ^{95}Mo (15.92%), ^{96}Mo (16.68%), ^{97}Mo (9.56%), ^{98}Mo (24.13%), ^{100}Mo (9.63%). Geochemically, Mo is classified as a siderophile element (Goldschmidt, 1930) with an experimentally derived metallic melt – silicate melt partition coefficient that likely exceeds 100 at oxygen fugitives relevant for core formation (e.g. Schmitt et al., 1989; Walter and Thibault, 1995; Wade et al., 2012). Molybdenum is also a moderately chalcophile element (Lodders and Palme, 1991), while it behaves as an incompatible element in silicate systems (Newsom and Palme, 1984). In fact, during mantle melting Mo shows geochemical similarities to the light rare-earth elements (Newsom and Palme, 1984; Newsom et al., 1986). As in documenting other mass-dependent isotopic variations, isotope ratios are commonly expressed as parts-per-thousand deviations from a standard. Over the last few years, NIST SRM 3134 has been used as a common reference material to enable inter-laboratory comparison (Goldberg et al., 2013; Nägler et al., 2014). The majority of laboratories have now adopted NIST SRM 3134 as a primary reference solution and, accordingly, the Mo isotope variations in this contribution are defined as

$$\delta^{98/95}\mathrm{Mo} = \left[\left(^{98}Mo/^{95}Mo_{\mathrm{sample}}\right)/\left(^{98}Mo/^{95}Mo_{\mathrm{NIST3134}}\right)\right]-1$$

and are expressed in ‰ (see Coplen, 2011).We note, however, that different isotope ratios (e.g. ^{97}Mo/^{95}Mo) and alternative normalisations have been used, relative to different purified Mo standard solutions, 'mean ocean water molybdenum' (Siebert et al., 2001) or more recently to a non-zero value of NIST SRM 3134 (see Greber et al., 2012). Where necessary, literature Mo isotope data reported in this study have been re-calculated to $\delta^{98/95}\mathrm{Mo} = 0$ for NIST SRM 3134.

Since Mo isotopic measurements have been widely used to study low temperature processes, a comprehensive range of chemical procedures has been developed over the past fifteen years mostly involving the use of anionic exchange resins for the separation of Mo (e.g. Anbar et al., 2001; Barling et al., 2001; Siebert et al., 2001; Malinovsky et al., 2005; Pietruszka et al., 2006; Archer and Vance, 2008; Pearce et al., 2009). More recently, some of these methods have been adapted (Pearce et al., 2009; Yang et al., 2015) or modified (Burkhardt et al., 2011; Burkhardt et al., 2014) to cope with higher matrix/Mo ratios commonly encountered in magmatic rocks. In particular, maintaining low blank levels is crucial to yield meaningful results, especially for magmatic samples depleted in Mo (i.e. mid-ocean ridge basalts). This is all the more important, given that chemical reagents as well as anionic exchange resins have been identified as major contributors to the overall analytical blank (Willbold et al., 2016). Simply scaling up chemical procedures that have been set up for processing Mo-rich samples may therefore lead to unacceptably high blank levels. Accordingly, approaches that minimise the resin volume and retain the capacity of processing large samples sizes (>0.1 g) are required.

The latter has been achieved by processing the samples over several cationic as well as anionic exchange resin steps to sequentially extract different matrix elements (Burkhardt et al., 2014) or by using unconventional chromatographic exchange resins, such as custom-prepared *N*-benzoul-*N*-phenylhydroxylamine (BPHA) resin (Li et al., 2014; Zhao et al., 2015). Alternatively, a single-pass anionic-exchange procedure has been developed that uses ascorbic acid to prevent retention of Fe on the resin, which otherwise interferes with Mo during the exchange reactions (Willbold et al., 2016). Overall, this wide range of procedures specifically tailored to the processing of magmatic rocks not only provides a valuable set of options for geochemists to chose from, it also demonstrates that the application of Mo isotopes to study planetary processes is on the verge of becoming a standard isotope system in isotope geochemistry.

In common with most of these procedures is the use of multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) combined with the double-spike method to determine mass-dependent variations of Mo (Siebert et al., 2001; Archer and Vance, 2008; Pearce et al., 2009; Burkhardt et al., 2014; Willbold et al., 2016) although sample-standard bracketing techniques have also been employed (e.g. Pietruszka et al., 2006). The double-spike method enables the robust and high-precision correction of instrument-induced isotope fractionation in natural samples (e.g. Dodson, 1963); a more recent review of the principles of the double-spike technique is given in (Rudge et al., 2009). The procedure involves the determination of at least three independent isotope ratios. For Mo, this allows a range of possibilities but studies have typically used a ^{97}Mo–^{100}Mo double spike, with the measurement of ^{97}Mo/^{95}Mo, ^{98}Mo/^{95}Mo and ^{100}Mo/^{95}Mo. Calculation of the isotopic compositions requires simultaneously solving three non-linear equations for their unknowns, i.e. the relative proportion of the double spike in the sample-double spike mixture, the mass fractionation occurring in the instrument during measurement of the spike-sample mixture as well as the natural fractionation factor of sample relative to the normalising reference solution (i.e. NIST SRM 3134).

Typically, a geological reference material is used to allow inter-laboratory comparison. For most other isotope systems (e.g. Nd, Sr, Hf), USGS geological reference materials, such as the Hawaiian basalt BHVO-2, represent appropriate, well-distributed and accessible reference materials. However, recent studies have shown that BHVO-2 is highly heterogeneous and enriched in terms of its Mo concentration, varying by several tens of per cent (Burkhardt et al., 2014; Li et al., 2014; Yang et al., 2015; Zhao et al., 2015; Willbold et al., 2016). This observation strongly suggests that BHVO-2 was contaminated with Mo during its preparation, which could have an adverse effect on its Mo isotopic homogeneity. While repeated measurements of $\delta^{98/95}$Mo in BHVO-2 appear to be much more reproducible than Mo concentration measurements (see Zhao et al., 2015), Willbold et al. (2016) noted a weak co-variation of Mo concentration with $\delta^{98/95}$Mo values probably related to mixing between the original rock composition and a contaminant, possibly steel abraded from crushing equipment during sample preparation. Fortunately, it appears the contaminant has a similar $\delta^{98/95}$Mo to the natural Mo in this basaltic sample (Willbold et al., 2016). Nonetheless, this extensive but variable contamination makes BHVO-2 an inappropriate geological reference material and may point to a more general problem for other isotope systems as has previously been well-documented for Pb (Woodhead and Hergt, 2000; Baker et al., 2004; Weis et al., 2005; Willbold and Jochum, 2005; Todd et al., 2015; Fourny et al., 2016). We therefore propose GSJ basalt JB-2 as an alternative, similarly accessible, yet more homogenous geological reference material for Mo isotope work in magmatic rocks (Freymuth et al., 2015; Zhao et al., 2015; Willbold et al., 2016).

Current methods dedicated to the analysis of Mo in magmatic rocks achieve reproducibilities of $\delta^{98/95}$Mo (i.e. 2SD uncertainty associated with the repeated analysis of a reference material) of <0.1‰, most of which range between 0.04 and 0.07‰. Given the total $\delta^{98/95}$Mo variation of ca. 1‰ in magmatic rocks (see below), these methods should provide enough resolution to resolve natural mass-dependent Mo isotope variations.

3. The effect of fractional crystallisation on the $\delta^{98/95}$Mo of magmatic rocks

Before mass-dependent Mo isotope variations in magmatic rocks can be interpreted as markers of distinct geochemical reservoirs, it needs to be assessed if crystallisation imposes a significant change in the Mo isotope composition of an evolving magmatic system melt. Mass-dependent isotope fractionation during magmatic differentiation has been documented for several metal isotope systems such as Fe (Schuessler et al., 2009; Teng et al., 2008), Si (Savage et al., 2011), Ti (Millet et al., 2016) and Zn (Chen et al., 2013). In general, the high incompatibility of Mo in most magmatic phases (e.g. Newsom and Palme, 1984) means that fractionation of Mo isotopes during fractional crystallisation should be very limited. Such an effect is likely restricted to magmatic systems involving phases with elevated Mo solid-melt partition coefficients.

3.1. Controls on magmatic isotopic fractionation

It is initially worth assessing in general whether or not there are changes in the bonding environment between Mo in the melts and in mineral phases that might be expected to result in isotopic fractionation. It has been shown that heavier isotopes concentrate in phases with stiffer and thus stronger bonds (Bigeleisen and Mayer, 1947; Urey, 1947) and that the stiffest bonds form around atoms with the lowest coordination and the highest valence state (Schauble, 2004). In silicate melts, the valence state of Mo decreases from +6 to +4 at an oxygen fugacity at around ΔIW −1 (Holzheid et al., 1994; O'Neill and Eggins, 2002; Farges et al., 2006). Thus Mo^{4+} species (MoO_3^{2-}) in silicate liquids were only likely to occur in the reduced terrestrial magma ocean environment during core formation (e.g. Hin et al., 2013). A compilation of the oxidation state of terrestrial basalts suggests that they have oxygen fugacities close to ΔIW +4 (Ballhaus et al., 1990; Wood et al., 1990; Bézos and Humler, 2005; Cottrell and Kelley, 2011). As such, Mo in terrestrial silicate melts should occur predominantly as tetrahedral Mo^{6+} species, MoO_4^{2-} (also see Candela and Holland, 1984; Holzheid et al., 1994; O'Neill and Eggins, 2002; Farges et al., 2006)

Details of the partitioning of Mo into magmatic minerals remain scarce. Adam and Green (2006) note that Mo plausibly fits on lattice strain parabola defined by Sb, Nb, and Ta in clinopyroxene and amphibole partitioning experiments, hinting a pentavalent oxidation state. This would require a different dominant valence state in solid and melt phases, as has been shown for magmatic partitioning of V (Righter et al., 2006). However, the dearth of hexavalent ions to define a lattice strain parabola means that the Mo data could also be argued to fit on a very tight parabola with W. Regardless, it appears that Mo is sited in the octahedral M1 (clinopyroxene) or M3 sites (amphibole) rather than replacing Si on a tetrahedral site. Molybdenum that is hosted in iron oxides and rutile (Bali et al., 2012; Greaney et al., 2016) must also occupy an octahedral site and indeed the ionic radius of octahedrally coordinated Mo^{6+} (59 pm) is close to that of Ti^{4+} (60.5 pm), which should make this a reasonably favourable substitution with coupled charge balancing reactions (such as $Ti^{4+} - Fe^{3+}$). Likewise, Mo incorporated into sulphide phases will be octahedrally coordinated. Thus, the coordination of Mo in likely magmatic mineral hosts is greater than for predominant tetrahedral Mo in melts, suggesting that most minerals should favour the lighter Mo isotopes. In the case of MoS_2 crystallising from magmatic fluids, notably isotopically light compositions relative to co-existing fluids are inferred for samples that grew during magmatically driven mineralisations (Hannah et al., 2007; Mathur et al., 2010; Greber et al., 2014). Stoichiometry constraints Mo to be tetravalent in MoS_2 whereas Mo should be predominantly hexavalent in common terrestrial melts and fluids (see above). Thus differences in valence as well as co-ordination may drive isotopic fractionation, favouring isotopically light Mo in the MoS_2. The same may be true if Mo in clinopyroxene and amphibole is pentavalent (Adam and Green, 2006). Although this initial analysis hints at the likely sense of isotopic fractionation, determining the magnitude of such effects requires experiments or a more detailed assessment of the bonding environment.

3.2. Magmatic Mo isotopic fractionation

Voegelin et al. (2014) investigated the variation of $\delta^{98/95}$Mo of a suite of clasts contained within the 161 ka Kos Plateau Tuff, Aegean Arc system. These xenoliths sample a full range of compositions (basaltic to rhyolitic) from prior magmatic activity. An overall positive correlation of Mo concentrations and SiO_2 content in this series of olivine basalts, andesites, dacites and rhyolites from Kos island (Fig. 1a) confirms the incompatible behaviour of Mo during magmatic differentiation (Voegelin et al., 2014). An increase in of $\delta^{98/95}$Mo from basalt to rhyolite is also evident in the same samples (Fig. 1b, c). Voegelin et al. (2014) further showed that the $\delta^{98/95}$Mo in hornblende and biotite minerals in the Kos magmatic suite are about 0.5‰ lighter than that of the coexisting dacitic melts (Fig. 2). Consequently, these authors postulated that fractional crystallisation of these isotopically light, hydrous phases could explain the observed trend towards heavier melt compositions with increasing degree of magmatic differentiation. Yet, on closer inspection, the trend towards heavier $\delta^{98/95}$Mo is defined by a sharp, step-like increase in $\delta^{98/95}$Mo at low Mo concentrations (ca. 1.7 μg g^{-1}; Fig. 1c) with the low Mo and $\delta^{98/95}$Mo side being defined by only two basaltic samples (see discussion below).

In contrast, a lack of Mo isotope fractionation was reported by Yang et al. (2015) for a suite of volcanic rocks from Hekla volcano, Iceland that also range from basalts to rhyolites (Fig. 1). Similar to the sample set from Kos, increasing Mo concentrations confirm the incompatible behaviour of Mo during magmatic differentiation. Yet, no correlation between $\delta^{98/95}$Mo and SiO_2 or Mo content was observed by Yang et al.

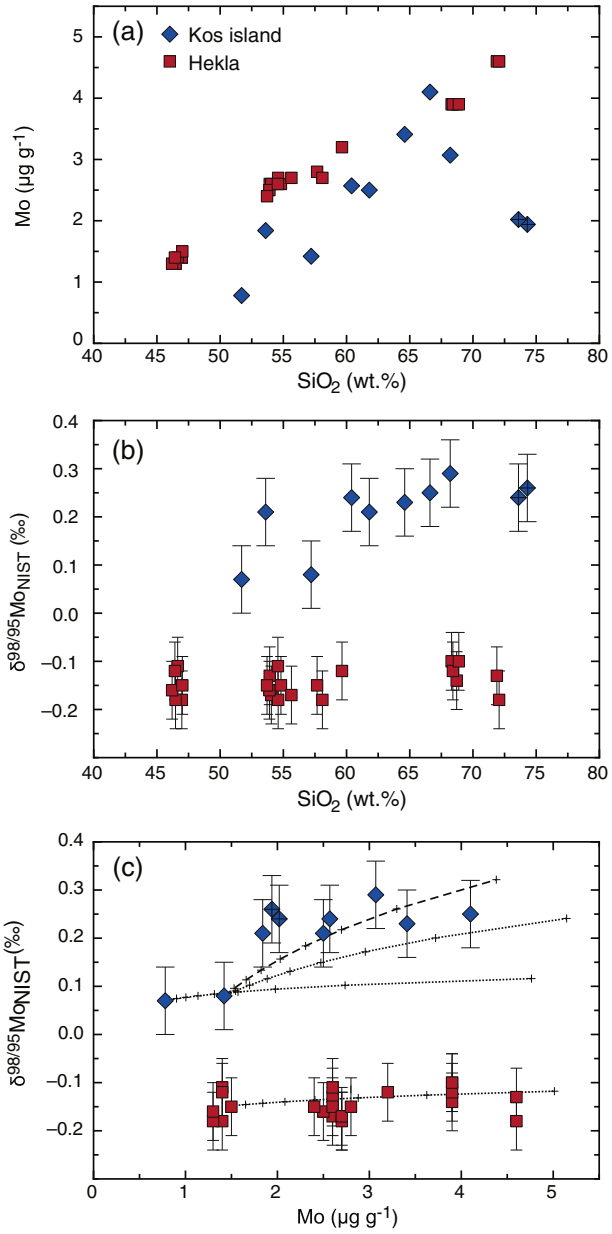

Fig. 1. Mo concentration and isotope data ($\delta^{98/95}$Mo) for two magmatic suites from Kos island (Aegean Arc system, Voegelin et al., 2014) and Hekla volcano (Iceland, Yang et al., 2015). (a) SiO_2 contents plotted against Mo concentrations (b) SiO_2 contents versus $\delta^{98/95}$Mo and (c) Mo concentrations versus $\delta^{98/95}$Mo. Two Kos rhyolitic pumice samples (believed to have lost Mo during fluid release) are marked with crosses. Several model crystallisation trajectories are illustrated using bulk D(Mo) of 0.2 (fine dashed lines) and 0.3 (coarse dashed line). Marks on the fractional crystallisation trends represent increments of 10% fractionation. The partition coefficients used correspond to the range appropriate to reproduce the Mo concentration co-variation with two highly incompatible elements (Cs for Kos and Rb for Hekla), assuming D = 0 for the highly incompatible elements. For the least evolved samples, fractional crystallisation using D(Mo) = 0.2 and $\alpha = 0.9999$ is used. These same values are consistent with the lack of discernible fractionation across the whole Hekla suite. For the Kos lavas we also show the fractionation trajectories with a change in fractionation assemblage in basaltic andesite compositions. We show two (steeper) differentiation paths using a more extreme $\alpha = 0.9995$, based on an average of the values determined for hornblende by Voegelin et al. (2014), both with the same (0.2) and a higher (0.3) bulk partition coefficient than used for initial crystallisation. The $\delta^{98/95}$Mo of the intermediate Kos lavas are still under-predicted using these values, which should maximise fractionation (hornblende is unlikely to represent 100% of the fractionation assemblage as necessary to generate the high α and besides the $D(Mo)_{hornblende}$ determined by Voegelin et al. (2014) was only 0.15). To mimic the Kos trend would require another phase to be involved. Although Voegelin et al. (2014) also invoke biotite, this becomes a liquidus phase only late during crystallisation and so cannot be the full explanation.

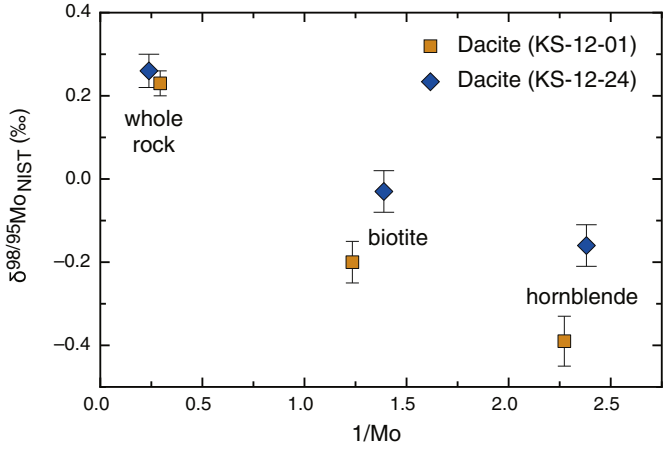

Fig. 2. The $\delta^{98/95}$Mo data of separated hydrous phases and felsic host rocks plotted against the inverse of their Mo concentrations for samples from Kos (Voegelin et al., 2014). The more fractionating hornblende phases contain consistently less Mo than biotites.

(2015), even though the Hekla lavas are argued to be sulphur saturated during fractional crystallisation (Moune et al., 2007). The latter resulted in a drop of sulphur content from 180 in the basalts to $<1\ \mu g\ g^{-1}$ in rhyolites, while Mo concentrations increased from ca. 1.3 to 4.6 $\mu g\ g^{-1}$ with no change in $\delta^{98/95}$Mo over the same range. Although Mo is considered a chalcophile element, Lodders and Palme (1991) pointed out that its partitioning into sulphides is strongly dependent on oxygen and sulphur fugacities and that D_{Mo} sulphide melt – silicate melt <20 are likely for typical magmatic systems, which is substantiated by more recent determinations (Li and Audétat, 2012). Given sulphur is a minor component in silicate melts and its modal fractionating abundance will be low (<1%), this should consequently not have a large effect on the Mo budget. Moreover, sulphur is also believed to be mobile and degassed as a volatile phase at Hekla, in keeping with many other volcanoes (Moune et al., 2007). Yang et al. (2015) pointed out the lack of a positive correlation between Mo and sulphur concentrations in the Hekla suite, which indeed points to a significant loss of sulphur by degassing rather than by fractionation of an immiscible sulphide melt.

To reconcile the lack of Mo isotope variation in the Hekla magmatic suite with the significant variation in Kos, Voegelin et al. (2014) and Yang et al. (2015) suggested that the water-undersaturated composition of the Icelandic magmas prevented stabilisation of the hydrous phases, which may have driven Mo isotopic fractionation in the subduction-related magmas from Kos island. Yet, Yang et al. (2015) also noted that establishing a truly co-magmatic relationship of the volcanic suite investigated is crucial for assessing the effect of magmatic differentiation on the isotope fractionation of Mo. Otherwise, it cannot be excluded that mixing of magmas with different $\delta^{98/95}$Mo compositions may mimic a magmatic evolution. Even in the relatively simple magmatic systems on Iceland, differentiation sequences typically involve magma mixing and crustal interaction, as noted for the popular Hekla suite (Sigmarsson et al., 1992). The situation can be considerably more complex for continental arc systems, such as the Aegean. Notably, Voegelin et al. (2014) report $^{87}Sr/^{86}Sr$ and $\varepsilon^{143}Nd$ data for their samples, which range between 0.7041 and 0.7047 and −0.3 to +1.6, respectively. Although the authors point out a lack of correlation between these two radiogenic isotope systems and $\delta^{98/95}$Mo values, the large range in radiogenic isotope ratios illustrates that these samples are not co-magmatic.

The majority of the Kos samples have a remarkably uniform Mo isotope composition ($\delta^{98/95}Mo = 0.23 \pm 0.03$‰; 2SD). Only two samples have consistently lower $\delta^{98/95}$Mo of 0.08‰ (±0.05‰; 2SD; Fig. 1c). As mentioned earlier, this results in an almost step-like increase in $\delta^{98/95}$Mo within a very narrow range of Mo concentration. Such a sharp change is hard to explain with fractionation crystallisation of

hornblende and biotite alone, since this transition occurs at the mafic end of the suite before these hydrous phases would be expected to be on the liquidus. We have illustrated this issue with some model fractionation scenarios in Fig. 1c. The Hekla samples can be reproduced with a bulk D_{Mo} of 0.2, assuming these anhydrous crystallising phases have a modest isotopic fractionation ($\Delta^{98/95}Mo_{melt\text{-}mineral} = +0.0001$) and this can also reproduce the first stage crystallisation in the Kos samples. Assuming hornblende becomes a liquidus phase at this point, we use a fractionation factor as determined by Voegelin et al. (2014) for hornblende ($\Delta^{98/95}Mo_{melt\text{-}hornblende} = 0.0005$) and two bulk D_{Mo} (0.2 and 0.3) compatible with the overall variability of Mo concentration relative to more highly incompatible elements (see figure caption) but slightly higher than measured for hornblende itself (Fig. 2). In these best-case examples, the isotopic differences between most mafic and evolved endmembers can be reasonably reproduced, but the intermediate lavas require a more complex petrogenesis. In all, this suggests that the range in $\delta^{98/95}$Mo values observed in the Kos sample set may have been caused by fractional crystallisation of hydrous phases but the involvement of genetically different magmatic systems or melt batches cannot be ruled out. As we discuss below, subduction zone processes can result in notable variability in $\delta^{98/95}$Mo and so distinguishing primary from secondary influences on $\delta^{98/95}$Mo in the Kos lavas is important but currently unresolved.

A less clearly defined case study of Mo isotope evolution during magmatic crystallisation is provided by the analyses of five lunar samples by Burkhardt et al. (2014), which show remarkably homogeneous $\delta^{98/95}$Mo (-0.05 ± 0.03‰; 2SE). These samples span a wide range of lunar compositions (KREEP, low-Ti and high-Ti basalts) that sample magmatic compositions from different stages of putative lunar magma ocean crystallisation. Given the potential importance of Fe-Ti oxides as a host for Mo, discussed above, the effects of ilmenite crystallisation and accumulation in these different lunar reservoirs might be expected to impart distinct Mo isotopic signatures. However, given the highly reduced state of the lunar mantle (i.e. below ΔIW −1, see Shearer et al., 2004; Shearer and Papike, 2004) Mo may be quantitatively present in its tetravalent form (Hin et al., 2013). Given Mo^{4+} is octahedrally coordinated in the melt rather than tetrahedrally, like Mo^{6+} (Farges et al., 2006), incorporation into Fe-Ti oxides may not have resulted in a change of bonding environment and thus may have well limited an isotope fractionation effect (see above).

4. The Mo isotope composition of arc rocks: implications for the solid Earth Mo cycle

In contrast to the rather subtle differences in $\delta^{98/95}$Mo imparted by the magmatic processes discussed above, mass-dependent fractionation of Mo isotopes due to changes in redox chemistry and bonding environment is particularly well expressed in low temperature environments (Fig. 3, Anbar, 2004). This has made the Mo isotope system an invaluable tracer in early paleo-oceanographic studies (Barling et al., 2001; Siebert et al., 2003; Anbar, 2004). The application of Mo isotopes as a paleo-redox proxy first required a sound characterisation of the current marine Mo cycle including seawater and its riverine input as well as that of potential sinks (e.g. McManus et al., 2002; Anbar and Rouxel, 2007; Archer and Vance, 2008). Under oxidizing conditions, Mo is inefficiently scavenged from seawater by adsorption onto iron-manganese oxyhydroxides leading to a large isotopic off-set of >2‰ in $\delta^{98/95}$Mo between seawater and pelagic clays (Fig. 3, Barling and Anbar, 2004; Tossell, 2005; Nägler et al., 2011). Under reducing conditions, however, near quantitative removal of Mo from the water column (Helz et al., 1996) results in euxinic sediments that have a $\delta^{98/95}$Mo indistinguishable from that of the oceans (Anbar, 2004; Nägler et al., 2011).

Recent studies have focussed on a better understanding of the secular rise of oxygen levels on Earth from Archean through Proterozoic times (e.g. Lyons et al., 2014). In particular, organic-rich sediments record an evolution from isotope fractionations of <1‰ $\delta^{98/95}$Mo in

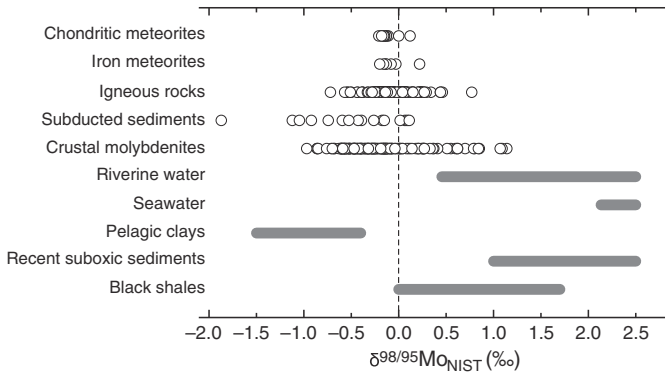

Fig. 3. Overview of Mo isotope data ($\delta^{98/95}$Mo) in sedimentary, magmatic and hydrothermal systems, as well as in meteorites. Modified from Anbar (2004). Data for igneous rocks updated and taken from Voegelin et al. (2014), Yang et al. (2015), Freymuth et al., 2015), König et al. (2016), Bezard et al. (2016), Zhao et al. (2015), Greber et al. (2015) and Willbold et al. (2016). Data for iron and chondritic meteorites from Burkhardt et al. (2014). Data for magmatic-hydrothermal molybdenites from Breillat et al. (2016). Data for subducted sediments from Freymuth et al. (2015).

Archean samples (Wille et al., 2013), ca. 2‰ $\delta^{98/95}$Mo throughout the Proterozoic (Wille et al., 2013; Kendall et al., 2015) to >3‰ $\delta^{98/95}$Mo in Phanerozoic and present-day marine sediments (Wille et al., 2013; Kendall et al., 2015). This has been interpreted to record reducing atmospheric conditions in the Archean followed by a rise in oxygen levels commonly attributed to the evolution of photosynthesing organisms. The latter culminated in the 'Great Oxidation Event' in the Paleoproterozic when the Earth's atmosphere and oceans reached oxidizing conditions (Wille et al., 2013). Such surface evolution likely results in changing subduction zone inputs with time and may thus influence the nature of mantle recycling.

The isotope fractionation under low- to moderate surface temperature conditions (>3‰ $\delta^{98/95}$Mo, Anbar, 2004) throughout most of the Earth's history exceeds those observed in magmatic systems (current average $\delta^{98/95}Mo = -0.08 \pm 0.46$‰, Siebert et al., 2003; Neubert et al., 2011; Voegelin et al., 2012; Burkhardt et al., 2014; Voegelin et al., 2014; Freymuth et al., 2015; Yang et al., 2015; Zhao et al., 2015; Bezard et al., 2016; König et al., 2016; Willbold et al., 2016). In particular, seafloor alteration is likely to affect the Mo isotope composition of crustal components in contact with low-temperature hydrothermal fluids (McManus et al., 2002; Freymuth et al., 2015). Thus, Mo isotopes could be a valuable tracer of recycled crustal material, which has inherited isotopically fractionated signatures from prior residence near the Earth's surface; i.e. following a concept similar to previous approaches using light isotope systems (e.g. Javoy et al., 1982; Chaussidon and Jambon, 1994; Eiler, 2001; Marty and Dauphas, 2003; Elliott et al., 2004; Bonifacie et al., 2008).

However, it is possible that subduction zone processes, in particular fluid dehydration of the subducting slab, fluid transfer and partial melting of the mantle, also impart important mass-dependent isotope fractionation effects on the recycled crustal material, e.g. similar to the effects observed for boron isotope systematics in magmatic arcs (e.g. Ishikawa and Nakamura, 1994; Peacock and Hervig, 1999; Wunder et al., 2005). As the majority of these processes occur under metamorphic to sub-solidus conditions they may lead to mass-dependent Mo fractionations that are significantly larger than those in magmatic systems, albeit smaller than those observed at near surface conditions.

An effective way of approaching this question is to characterise the Mo inventory of the subducted plate and compare this with that of the volcanic material added to the volcanic arc system. Freymuth et al. (2015) analysed the Mo isotope composition and concentrations in representative sections of the upper oceanic crust (from ODP sites 801 and 1256), including samples of sediments, currently being subducted beneath the Mariana arc system (Fig. 3) and compared these with Mo isotope data for well-characterised Mariana arc basalts. The Mariana

arc lavas are enriched in Mo compared to elements of similar compatibility during upper mantle melting (i.e. Ce and other light rare-earth elements) and have a $\delta^{98/95}$Mo composition ca. 0.3‰ higher than the unaltered mafic oceanic crust samples analysed in the same study (Fig. 4). Freymuth et al. (2015) also showed that the subducted sedimentary lithologies host isotopically light Mo in keeping with previous studies of oceanic sediments (e.g. Anbar, 2004, see Fig. 4). The top few hundred metres of the mafic crust have a $\delta^{98/95}$Mo significantly heavier than its lower sections, which have a rather remarkably uniform Mo isotope composition. Freymuth et al. (2015) suggested that the isotopically heavy top part of the crust formed by alteration with seawater carrying an isotopically heavy Mo signature (Fig. 3).

The relative enrichment of Mo over Ce in Mariana arc lavas argues against partial melting as the main process of adding Mo to the Mariana arc crust. Experimental results show that Mo is readily mobilised in subduction zone fluids (as an oxidized MoO_4^{2-} species) with a solubility comparable to that of other "fluid-mobile" elements such as U (König et al., 2008; Bali et al., 2012). Similarly, Freymuth et al. (2015) observed a positive correlation of Ce/Mo and Ce/Pb ratios for their Mariana arc lavas and suggested a common source for both fluid-mobile elements, Mo and Pb. Available Pb isotope data for Mariana arc basalts suggests that the Pb (and by analogy the isotopically heavy Mo) budget in the Mariana arc lavas is entirely derived from the subducting Pacific plate rather than from the mantle wedge of Indian mantle affinity (Freymuth et al., 2015). Moreover, the Pb isotopic signature did not have the distinct enrichment of $^{206}Pb/^{204}Pb$ that would be anticipated for Pb derived from the uppermost, altered mafic crust.

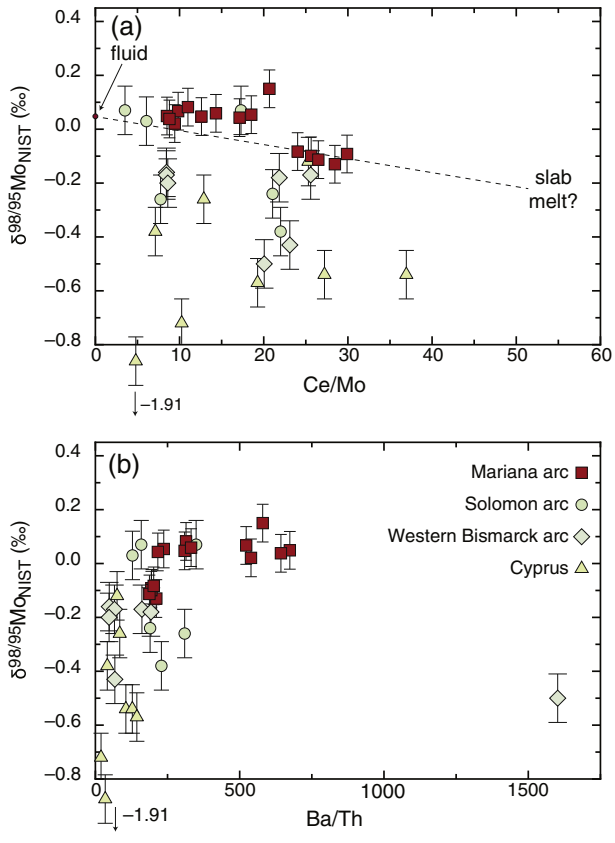

Fig. 4. Mo isotope data ($\delta^{98/95}$Mo) plotted against (a) Ce/Mo and (b) Ba/Th ratios for arc-related basalts from the Mariana arc, the Solomon arc, Cyprus as well as Papua New Guinea (Freymuth et al., 2015; König et al., 2016). Samples with high Ba/Th and low Ce/Mo are assumed to contain a slab-derived fluid component (with high $\delta^{98/95}$Mo), whereas basalts with low Ba/Th, low $\delta^{98/95}$Mo and high Ce/Mo may contain a slab melt component. Note that while such a systematic may be seen in Ba/Th versus $\delta^{98/95}$Mo (b) as suggested by König et al. (2016) it is less well obvious in Ce/Mo versus $\delta^{98/95}$Mo for the West Bismarck arc and Cyprus systems, possibly indicating the geological and geochemical complexity of these arc-related settings (see text).

Although the top few hundred metres of the subducted oceanic crust analysed by Freymuth et al. (2015) are characterised by high $\delta^{98/95}$Mo values, the high-precision Pb isotope measurements of Freymuth et al. (2015), supported by Pb and Sr isotope observations of Avanzinelli et al. (2012), argue against an origin of the fluids from the top part of the subducted crust. Rather, these authors suggested that the fluid is most likely derived from the cooler, less altered portion of the subducted slab. Such a model requires that the heavy Mo isotope composition observed in the Mariana arc lavas must be the result of isotope fractionation during dehydration and fluid flow within the slab rather than being representative of one or several lithological components of the subducted lithosphere.

Similarly, König et al. (2016) argued that the range of $\delta^{98/95}$Mo values observed in arc-related volcanic rocks from the Solomon arc, Western Bismarck arc (Papua New Guinea) and Cyprus results from the variable addition of slab-derived components to the sub-arc mantle wedge (Fig. 4). In line with the interpretation by Freymuth et al. (2015), König et al. (2016) suggested that high $\delta^{98/95}$Mo values in arc-related rocks that are associated with high Ba/Th ratios (i.e. some of their Solomon arc samples) are due to the addition of a slab-derived fluid component. Like the Mo-Ce elemental pair, Ba is assumed to be more mobile in slab-fluids compared to Th, which otherwise partitions like Ba during mantle melting (e.g. Elliott, 2003). König et al. (2016) also noted that their samples with low Ba/Th, potentially more dominated by a sediment component, had low $\delta^{98/95}$Mo signatures (i.e. mainly samples from the Bismarck arc and Cyprus).

In their favoured model, Freymuth et al. (2015) proposed that residual minerals in the slab retain light Mo isotopes from fluids passing through the oceanic crust during slab dehydrations. One possible mechanism could be the equilibration of these fluids with rutile, which is a common metamorphic phase in metabasalts and metagabbros, where rutile has been shown to react with fluids in eclogite veins (Spandler et al., 2011). Experimental data suggests that rutile incorporates Mo at 2.6GPa and 600–800 °C with rutile-fluid partition coefficients ranging between 1.25 and 24 close to the ΔIW +4 (Bali et al., 2012), much higher than those observed for other elements (e.g. ≪0.25 for Ce, Stalder et al., 1998). Assuming that residual rutile preferentially incorporates light Mo isotopes by equilibration with dehydration-derived fluid (compare with above), such a process could explain the high $\delta^{98/95}$Mo signatures observed in arc-related rocks that show strongest evidence of a fluid component.

The influx of fluid released from the oceanic slab into the top part of the subducted oceanic lithosphere may also trigger melting at the sediment-mantle wedge interface (Nichols et al., 1994; Johnson and Plank, 1999). Building on this model, König et al. (2016) suggested that the break-down of minor amounts of sediment-hosted rutile during sediment melting and the release of the light Mo isotopes previously acquired during equilibration with dehydration fluid could explain the trend in $\delta^{98/95}$Mo and Ba/Th ratios observed for arc-related rocks (Fig. 4). Nevertheless, Freymuth et al. (2015) reported marine sediment with $\delta^{98/95}$Mo as low as −1.9‰ (Fig. 3), even though the averaged Mariana sediment package has less extreme $\delta^{98/95}$Mo (i.e. $\delta^{98/95}$Mo ca. −0.29‰). It is thus not clear that subducted sediments need to be additionally fractionated by this process in order to explain the lower values of $\delta^{98/95}$Mo (ca. −0.4 to −0.7‰) in the western Bismarck arc and Cyprus samples. Moreover, König et al. (2016) do not report Mo isotope data for oceanic sediments involved in these three subduction systems to allow this issue to be assessed in more detail; not least because such sediments are no longer exposed in the cases of the Western Bismarck arc and the Miocene Cyprus system. All three settings studied by König et al. (2016) are geologically and geochemically complex arc-related systems and not necessarily representative of global arc processes. Indeed the sample set includes a number of boninitic magmas, unusual rocks that are typically found in the fore-arc regions

of subduction zones and that are believed to be fluid-rich melts of highly depleted mantle often associated with the onset of subduction (Hickey and Frey, 1982; Crawford et al., 1989; Cooper et al., 2010; König et al., 2010). A further consideration with the dataset of König et al. (2016) is that many samples have notable loss-on-ignition values (up to 5 wt.%). Given $\delta^{98/95}$Mo is very susceptible to the effects of weathering (see above), this casts doubts on the primary nature of some of the isotopic variations. Whether or not the Solomon arc, the Western Bismarck arc and the Miocene Cyprus system are suited as type locations to establish a globally applicable model for the Mo isotope system, as suggested by König et al. (2016), thus remains unclear. It is also worth noting that the suite of arc lavas from Kos, studied by Voegelin et al. (2014) to examine the behaviour of Mo during differentiation, are derived from basalts with relatively high $\delta^{98/95}$Mo, as can be seen in comparison to the Icelandic samples of Yang et al. (2015) (Fig. 1). These isotopically heavy compositions are in keeping with the observations of Freymuth et al. (2015), even if the Kos lavas contain a greater sedimentary/crustal component given their very unradiogenic Nd isotope and radiogenic Sr isotope composition (see above).

In summary, presently available data for Mo isotope systematics in arc-related rocks suggest that the Mo isotope compositions of the volcanic arc may not directly match input compositions into the arc system. Rather, they may be dominated by a fluid component, possibly modified by sediment melt contribution, that has acquired its heavy Mo isotope composition through interaction with the subducted mafic crust. Although the topmost few hundred metres of the subducted lithosphere are characterised by notable mass-dependent variations of Mo isotope ratios (seawater alteration and the presence of sediments), mass balance considerations suggest that the Mo isotope budget of the subducted slab in the Mariana subduction zone is dominated by that of unaltered oceanic crust (Freymuth et al., 2015). When considering Mo fluxes into and out from the Mariana arc system, ca. 35% of Mo is lost from the subducting slab as a whole to the arc system. Dehydration and equilibration with residual phases such as rutile within the oceanic crust, most likely cause the release of predominantly heavy Mo from the slab. Thus, depending on the total amount of Mo released during subduction, the Mo isotope composition of the residual slab that is recycled into the deeper mantle must be as light or lighter than that of the subducted oceanic crust (Freymuth et al., 2015). In all, both major components of the deep recycled crust should carry isotopically light Mo.

5. The Mo isotope composition of geological reservoirs

5.1. Chondrites and the terrestrial core

A sound characterisation of the composition of primitive meteorites and their components is important for our understanding of the bulk composition of terrestrial planets. Although the generic model of a chondritic bulk Earth composition has recently been challenged (e.g. Bourdon et al., 2008; O'Neill and Palme, 2008; Campbell and O'Neill, 2012; Bonsor et al., 2015), establishing the Mo isotope composition of chondritic meteorites provides a valuable baseline for the investigation of the Mo isotopic composition of terrestrial geochemical reservoirs, such as the core, the mantle and the crust. Within meteorites, the distribution of Mo is mainly controlled by its affinity for metal phases as well as by its refractory character leading to enrichments in calcium-aluminium-rich inclusions (e.g. Burkhardt et al., 2014). On a planetary scale, Mo strongly partitioned into the Earth's core and is highly depleted in the mantle (Newsom and Palme, 1984; Newsom, 1985; Newsom et al., 1986; Walter and Thibault, 1995; Righter et al., 1998; Holzheid and Palme, 2007; Wade et al., 2012).

High-precision Mo isotope measurements of ten chondrites and four magmatic iron meteorites revealed a remarkably homogeneous bulk Mo isotope composition of the inner solar system with an average $\delta^{98/95}$Mo of -0.16 ± 0.02‰ (2SE, see Burkhardt et al., 2011), despite a variable s-process component between different meteorite groups (Dauphas et al., 2002; Burkhardt et al., 2011). Exceptions are CM and CK chondrites that are displaced towards higher $\delta^{98/95}$Mo values. In their preferred model Burkhardt et al. (2014) suggested that evaporative loss of isotopically light Mo (as MoO_2) shifted the bulk composition of these two chondrite groups towards heavier $\delta^{98/95}$Mo composition, although it is possible that heterogeneous distribution of refractory phases in the analysed samples plays a role. The common Mo isotope composition of the majority of chondrites and magmatic iron meteorites is in line with the highly siderophile character of Mo. The latter causes near-quantitative concentration of Mo in the metallic core of planetary bodies thus closely approximating the $\delta^{98/95}$Mo of the bulk parent body. This common $\delta^{98/95}$Mo composition indicates that the bulk composition of the inner Solar system as well as that of terrestrial planets is most likely represented by the average chondritic composition of $\delta^{98/95}\text{Mo} = -0.16 \pm 0.02$‰ (Burkhardt et al., 2014).

5.2. Bulk silicate Earth

The variation of currently available Mo isotope data for igneous rocks (Fig. 3) most likely resulted from terrestrial isotopic fractionation processes such as described in the previous two sections. Such variability potentially hampers the establishment of a representative Mo isotope composition of the bulk silicate Earth from direct measurements of mantle-derived melts. Hin et al. (2013) experimentally documented a preferential partitioning of light Mo isotopes into the metal phase, which thus predicts an elevated $\delta^{98/95}$Mo composition of the residual bulk silicate mantle. This sense of fractionation is in keeping with the change of redox and bonding environment for a high valence cation, as also demonstrated for Si (Shahar et al., 2009; Hin et al., 2013). In these experiments, carried out under reduced conditions, Mo is most likely present as Mo^{4+} the silicate melt phase, while in the metal it occurs in its elemental form. Hin et al. (2013) constrained the equilibrium fractionation of Mo isotopes between the metal and the silicate melt phases over a range of temperature and oxygen-fugacity. These experiments showed that Mo isotope fractionation varied little with oxygen fugacity but inversely with temperature, as would be expected. Given this relationship, Burkhardt et al. (2014) suggested a maximum offset of $\Delta^{98/95}\text{Mo}_{\text{Silicate - Metal}}$ of ca. 0.3‰ between the bulk silicate Earth and the core at T = 1000 °C, which Burkhardt et al. (2014) assumed as the minimum temperature of core formation; although realistic values are likely to be much higher (Chabot et al., 2005; Wood et al., 2006; Rubie et al., 2007; Righter, 2011; Siebert et al., 2011; Mann et al., 2012; Siebert et al., 2012; Wade et al., 2012; Siebert et al., 2013) such that $\Delta^{98/95}\text{Mo}_{\text{Silicate-Metal}} \sim 0.05$‰ is more plausible. Assuming a chondritic $\delta^{98/95}$Mo value for the core (see above), a bound of $\delta^{98/95}$Mo ca. +0.14‰ is placed in the maximum value of bulk silicate Earth, while a value of ~ −0.10‰ is more likely (Fig. 5).

An independent constraint on the maximum $\delta^{98/95}$Mo value of the Earth-Moon system comes from the Mo isotope composition of five lunar samples measured by Burkhardt et al. (2014). These samples represent different lunar geochemical reservoirs (see above) and average at $\delta^{98/95}\text{Mo} = -0.05 \pm 0.03$‰ (2SE), thus distinctly heavier than the $\delta^{98/95}$Mo chondritic value of −0.16‰. Given indistinguishable lunar and terrestrial compositions in other isotopic systems, e.g. oxygen (Young et al., 2016), titanium (Zhang et al., 2012) and silicon (Armytage et al., 2012), it might be expected that the same would be the case for Mo. The influence of possible Mo loss and fractionation during the giant impact volatilisation (O'Neill, 1991) seems unlikely given its refractory nature and insignificant effects for more volatile and lighter elements such as Li and Si (Magna et al., 2006; Armytage et al., 2012; Fitoussi and Bourdon, 2012). A more significant consideration is fractionation during lunar core formation. Assuming that the Moon has a metallic core (Weber et al., 2011) with a chondritic $\delta^{98/95}$Mo composition, a value of $\Delta^{98/95}\text{Mo}_{\text{Silicate - Metal}}$ of 0.11 ± 0.04‰ for the lunar core-mantle system accounts for the silicate $\delta^{98/95}$Mo of the Moon (Burkhardt et al.,

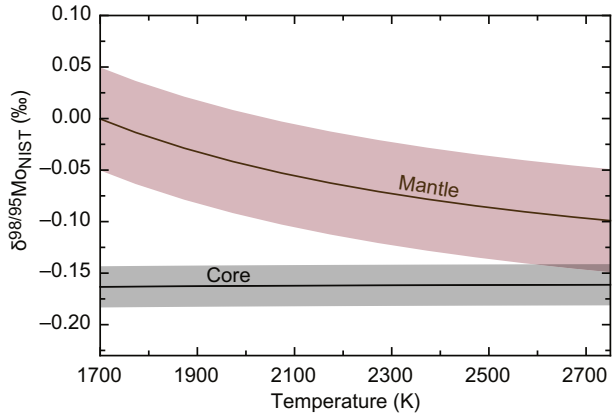

Fig. 5. Modelled bulk silicate Earth Mo isotope composition assuming bulk core formation and equilibrium Mo isotope fractionation between silicate mantle and metallic core as a function of temperature (Hin et al., 2013). Model assumes chondritic bulk composition of the Earth (Burkhardt et al., 2014) and a $D(Mo)_{Metal\ -\ Silicate}$ of 100. Red shaded area represents current state-of-the-art uncertainty of $\delta^{98/95}$Mo measurements (2SD 0.05‰). Grey shaded area represents uncertainty of $\delta^{98/95}$Mo of core based on that of measured chondrite data (0.02‰, Burkhardt et al., 2014).

2014). This translates into a metal-silicate equilibration temperature of 2070 ± 200 K (see Hin et al., 2013), which is in good agreement with the temperature estimated based on the metal-silicate partitioning of other siderophile elements within the lunar mantle (Righter, 2002). A more detailed model of lunar mantle $\delta^{98/95}$Mo requires consideration of equilibration between Earth and Moon, appropriate partitioning coefficients, as well as temperature of core formation. However, lunar core formation provides a compelling means to account for lunar samples having higher $\delta^{98/95}$Mo than anticipated for bulk silicate Earth (Fig. 5).

It s difficult to account for relative mantle abundances of the two refractory siderophile elements, Mo and W, using metal-silicate partitioning experiments, which consistently over-predict terrestrial mantle Mo/W (Wade et al., 2012). This discrepancy of Mo content in the bulk silicate Earth could be reconciled if a change in the S/Fe ratio of material added to the Earth during the final stages of core formation is invoked (Wade et al., 2012; Rubie et al., 2016). There are no experiments to assess if this final phase of Mo removal changes the isotopic fractionation, although given the similarity in bonding environment, the sense of fractionation should be the same. A further consideration is the impact of the late veneer, which has been suggested to shape the modern W isotope composition of the majority of the mantle since the late-Archean (Willbold et al., 2011; Touboul et al., 2015; Willbold et al., 2015). Given metal-silicate partition coefficient of 100 for Mo and simple batch core-mantle equilibration, a 0.5% by mass late veneer would account for ~20% of modern mantle Mo. The isotopic effect of the late veneer is limited, however, given the modest contrast between the Earth's mantle post core formation and a chondritic veneer. For example, assuming a mantle set by a high temperature (2700 K) core-mantle equilibrium (Fig. 5), the bulk silicate Earth $\delta^{98/95}$Mo changes from −0.10 to −0.11‰ as a result of the late veneer.

5.3. The depleted mantle

An initial constraint of $\delta^{98/95}$Mo for the depleted mantle source came from the measurement of five least-altered samples of oceanic crust from ODP site 1256 (Freymuth et al., 2015). These samples give a consistent $\delta^{98/95}$Mo value of −0.20 ± 0.06‰ (2SE). Although even these samples are possibly affected by minor degrees of alteration, this value is consistent with the range in $\delta^{98/95}$Mo (from −0.15 to −0.25‰) for hand-picked mid-ocean ridge basalt glasses (Hibbert et al., 2013).

More recently, Bezard et al. (2016) reported $\delta^{98/95}$Mo compositions for volcanic glasses from the Pacific-Antarctic and the Mohns-Knipovich ridge, ranging from −0.24 to +0.15‰. Major element variations for each of these segments suggest that these samples were produced by different degrees of partial melting of the mantle source. The absence of correlation between $\delta^{98/95}$Mo and indices for partial melting (i.e. Na_8, Klein and Langmuir, 1987) or magma differentiation (i.e. MgO content) suggest a negligible effect of these processes on the isotope variations observed (Section 3). Similarly, $\delta^{98/95}$Mo values for the samples are not correlated with common indices of seafloor alteration or in-situ assimilation of sulphide-bearing crust, such as elevated Cl/K ratios or elevated δ^{34}S values. Rather, the highest values of $\delta^{98/95}$Mo ratios are found in samples with the most enriched signatures in terms of radiogenic isotope systems (i.e. low $^{143}Nd/^{144}Nd$ and high $^{87}Sr/^{86}Sr$) suggesting that their mantle sources may contain a component with a high $\delta^{98/95}$Mo. In contrast, samples with the lowest $\delta^{98/95}$Mo values, highest $^{143}Nd/^{144}Nd$ and lowest $^{87}Sr/^{86}Sr$ ratios may represent the Mo isotope composition of the uncontaminated depleted mantle source. The five samples with the highest $^{143}Nd/^{144}Nd$ ratios (from 0.51317 to 0.51327) have a mean $\delta^{98/95}$Mo of −0.21 ± 0.02‰ (2SE). This is in very good agreement with the earlier estimate of −0.20 ± 0.06‰ (Hibbert et al., 2013; Freymuth et al., 2015). From these data it appears that the depleted mantle has a slightly sub-chondritic Mo isotope composition, albeit with a range to some heavier values.

5.4. The continental crust

Given its accessibility, it is perhaps ironic that the continental crust is so far the least well-characterised geochemical reservoir in terms of its Mo isotope composition. For many fluid-immobile elements (i.e. rare-earth elements, see Taylor and McLennan, 1985), shale sediments have proven to be very efficient in estimating the bulk composition of the upper continental crust, given the averaging effect of bedrock erosion and sediment mixing during transport and deposition. Yet, Mo is a fluid mobile element and is affected by isotope fractionation during weathering, riverine transport and deposition, such that the range in $\delta^{98/95}$Mo in sediments is far larger than so far observed in magmatic rocks (see Fig. 3 and Barling et al., 2001; Siebert et al., 2003; Anbar, 2004; Arnold et al., 2004; Barling and Anbar, 2004; Malinovsky et al., 2007; Archer and Vance, 2008; Pearce et al., 2008; Gordon et al., 2009; Scheiderich et al., 2010; Nägler et al., 2011; Neubert et al., 2011; Goldberg et al., 2012; Voegelin et al., 2012; Xu et al., 2012).

Molybdenum is very efficiently mobilised from crustal source rocks and enriched in hydrothermal fluids (Keppler and Wyllie, 1991; Audétat and Pettke, 2003; Zajacz et al., 2008; Audetat, 2010). The Mo isotope compositions of hydrothermally-derived molybdenites that result from this process have been used to estimate the Mo isotope signature of the continents (Arnold et al., 2004; Dahl et al., 2011; Czaja et al., 2012). Although an attractive idea, recent studies have found a variability of >2‰ in $\delta^{98/95}$Mo for molybdenites (see recent compilation in Breillat et al., 2016), again, much larger than the range observed for magmatic rocks (Fig. 3). It is thus unlikely that this range reflects the $\delta^{98/95}$Mo variability of crustal host-rocks, from which these hydrothermal fluids derived from. Higher $\delta^{98/95}$Mo of molybdenites precipitated from later stage fluids, as gauged from other chemical (e.g. Re abundances, Hannah et al., 2007; Mathur et al., 2010) or geological (e.g. inclusion temperatures, Greber et al., 2014) proxies, suggests that fractional removal of isotopically light molybdenite from evolving mineralising fluids is an important process in generating this $\delta^{98/95}$Mo variability. Tossell (2005) calculated that, at ambient room temperature, aqueous Mo sulphide complexes have $\delta^{98/95}$Mo >2‰ lighter than MoO_4^{2-} complexes. Although molybdenite formation occurs at significantly higher temperature in more complex fluids, this sense of fractionation is appropriate to explain these observations. However, the wide variability of $\delta^{98/95}$Mo in molybdenite observed both on a local scale and between different deposits worldwide (Mathur et al., 2010; Breillat et al., 2016) requires processes in addition to Rayleigh fractionation to account for the full range of isotopic compositions (Mathur et al., 2010; Greber et al., 2011; Greber et al., 2014; Breillat et al., 2016)

These studies demonstrate that the isotopic composition of molybdenites provide a noisy record of the $\delta^{98/95}$Mo of the upper continental crust. Hannah et al. (2007) suggested that in a Rayleigh fractionation scenario, an average composition of molybdenite compositions for a given locality should be representative of the source. On this basis, the average Mo isotope composition for ca. 240 molybdenite samples (Fig. 6), for which $\delta^{98/95}$Mo data normalised to NIST SRM 3134 are available (Greber et al., 2014; Breillat et al., 2016) provides a loose bound on the composition of the continental crust. Arguing that molybdenite forming fluids are fractionated from their source rock, Greber et al. (2014) proposed their mean molybdenite $\delta^{98/95}$Mo of ca. +0.15‰ to represent a maximum composition of the upper continental crust. The compiled molybdenite data shown in Fig. 6 has a mean $\delta^{98/95}$Mo of −0.04‰ ± 0.84‰ (2SD), lower than the estimate provided by Greber et al. (2014). This may reflect variability in samples, but the study by Breillat et al. (2016), on which the dataset shown in Fig. 6 is largely based on, used a sample-standard bracketing technique, which is more prone to inaccuracy than the double-spike approach of the former study.

Another constraint on the $\delta^{98/95}$Mo composition of the continental crust comes for the assumption that its bulk compositions is andesitic (Wedepohl, 1995; Rudnick and Gao, 2004) and matches that of average arc crust (Taylor, 1967; Taylor and McLennan, 1985). Using their own and previous data for arc-related basalts from Kamchatka (Siebert et al., 2003), Voegelin et al. (2014) suggested a preliminary average $\delta^{98/95}$Mo between +0.05 and +0.15‰ for the upper continental crust based on subduction-related volcanic rocks. There are now more data available (see previous section), but this estimate is in keeping with most analyses of unaltered samples. A more robust figure will require a comprehensive study of much larger number of subduction zone systems.

Overall, the current data suggest a super-chondritic $\delta^{98/95}$Mo composition of the upper continental crust. This is in keeping with a sub-chondritic, depleted mantle (Section 5.3) and the long-held notion that continental crust and depleted mantle are complementary reservoirs (DePaolo, 1979; O'Nions et al., 1979; DePaolo, 1980; Jacobsen and Wasserburg, 1980; Hofmann, 1988). We examine a simple mass-balance model, to look at the consequences of our preliminary constraints on the $\delta^{98/95}$Mo of continental crust ($\delta^{98/95}Mo_{CC}$). Namely, we approximate (Table 1):

$$\delta^{98/95}Mo_{CC} = \delta^{98/95}Mo_{BSE} + X_{RM}/(1-X_{RM}) \times 1/D_{Mo} \times \left(\delta^{98/95}Mo_{BSE} - \delta^{98/95}Mo_{DM}\right) \quad (1)$$

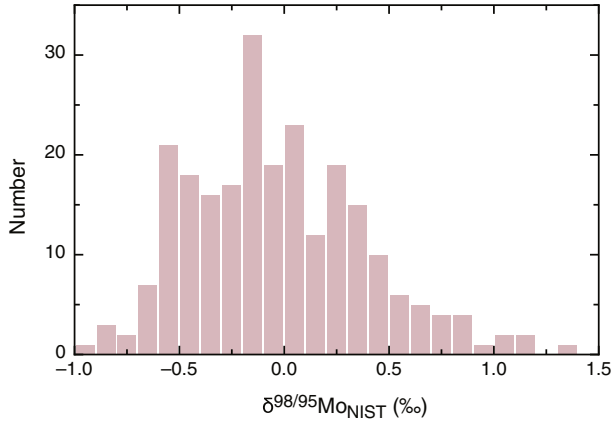

Fig. 6. Distribution of $\delta^{98/95}$Mo in continental molybdenites, for which Mo isotope data normalised to NIST SRM 3134 are available (Greber et al., 2014; Breillat et al., 2016). Average $\delta^{98/95}$Mo of the 240 samples is −0.04 ± 0.84‰ (2SD). See text for discussion.

D_{Mo} is the ratio of Mo concentrations in the continental crust and the depleted mantle. Values of 0.8 μg g^{-1} and 0.025 μg g^{-1} from Salters and Stracke (2004) and Rudnick and Gao (2014) respectively yield D_{Mo} = 32. Note that recent isotope dilution values for mid-ocean ridge basalts Bezard et al. (2016) give consistent values of 0.02 to 0.03 μg g^{-1} for the depleted mantle, assuming they represent 10% melting of the upper mantle. X_{RM} is the mass fraction of residual mantle in the continental crust (CC) – depleted mantle (DM) system. This gives the fractional mass of depleted mantle (X_{DM}) in the mantel as a whole by

$$X_{DM} = (m_{crust}/m_{mantle}) \times [X_{RM}/(1-X_{RM})] \quad (2)$$

where m_{crust} and m_{mantle} are the absolute masses of the crust (2×10^{25} g) and the mantle (4×10^{27} g). Inserting Eq. (2) into Eq. (1) yields

$$\delta^{98/95}Mo_{CC} = \delta^{98/95}Mo_{BSE} + X_{DM}/(m_{crust}/m_{mantle}) \times 1/D_{Mo} \times \left(\delta^{98/95}Mo_{BSE} - \delta^{98/95}Mo_{DM}\right) \quad (3)$$

As with its $\delta^{98/95}$Mo, the Mo concentration of the bulk continental crust requires further investigation, but by using D_{Mo} ranging between 20 and 40 we hope to encompass reasonable uncertainty on this value. We use two values of $\delta^{98/95}Mo_{BSE}$, the chondritic average of Burkhardt et al. (2014), $\delta^{98/95}Mo_{BSE\_1} = -0.16 \pm 0.02$‰ and another assuming that the $\delta^{98/95}$Mo of the silicate Earth after core formation is represented by the lunar mantle; i.e. −0.05 ± 0.03‰, which is followed by a late accretion of chondritic material (a 'late veneer' of 0.5% by mass; see above), i.e. $\delta^{98/95}Mo_{BSE\_2} = -0.08 \pm 0.03$‰. These two estimates should bracket likely values for $\delta^{98/95}Mo_{BSE}$. Finally, $\delta^{98/95}Mo_{DM} = -0.21 \pm 0.02$‰ (Bezard et al., 2016) is taken as an estimate for the depleted mantle. The results of these mass balance calculations are shown in Fig. 7.

The super-chondritic values of $\delta^{98/95}Mo_{CC}$, tentatively inferred above, are consistent with current notions that the continents are sourced from a mass of mantle somewhat greater than the upper mantle, e.g. Stracke et al. (2003a). The significant isotopic difference between the continental crust and the mantle, as observed at subduction zones (Section 3) and a sufficiently high concentration of Mo in the continental crust, seems to lead to a discernible continental crust – mantle complementarity in Mo isotopes. This is the first mass-dependent isotope system to show this behaviour and if the input values for Eq. (3) can be adequately refined from the current rudimentary values, this may place new perspectives on the volume of the melt-depleted mantle reservoir.

The current estimates of $\delta^{98/95}Mo_{CC}$ come from young, uppermost crust. Yet, it is well documented that the continental crust is very heterogeneous in terms of its isotopic as well as its chemical composition (Rudnick and Gao, 2014), not least owing to fluid-related transport of elements between the lower and the upper continental crust. Since Mo is sensitive to mobilisation in magmatic fluids neither the upper nor the bulk continental crust can be regarded as homogeneous. Such processes may result in some of the surprisingly low Mo concentrations measured in crustal rocks (0.16 to 0.85 μg g^{-1}, Greaney et al., 2016). Fluid mobilisation will likely influence not only Mo concentration but also $\delta^{98/95}$Mo, as inferred by Greber et al. (2014) for crustal systems and Freymuth et al. (2015) for the subducting slab. Moreover, on geological timescales, continuous re-melting of pre-existing lower mafic arc crust during orogenic events was accompanied by the release of likely isotopically heavy fluids into higher crustal levels. In the same context, the role of magmatic fractionation of (isotopically light) sulphide phases during melt differentiation in the crust of a continental arc setting may impart a significant Mo isotope effect on the residual melt and thus the upper crust (Jenner et al., 2010). Assuming that the continental crust formed in arc settings, both processes (fluid release and sulphide fractionation) may thus have contributed to the evolution of the Mo isotope system of the bulk continental crust towards a super-

Table 1
Suggested preliminary Mo isotope composition of terrestrial reservoirs. Uncertainties as 2SE for $\delta^{98/95}$Mo and 1 SD for concentrations.

Reservoir	Chondrites	Core	Bulk silicate Earth	Depleted mantle	Continental crust
Mo [μg g^{-1}]	1.33 ± 0.20[a]	ca. 5[b]	0.047 ± 0.019[c]	0.025 ± 0.007[d]	ca. 0.8[e]
$\delta^{98/95}$Mo [‰]	−0.16 ± 0.02[a]	−0.16 ± 0.02[a]	−0.16 ± 0.02[f]	−0.21 ± 0.02[g]	<+0.15[f,h]

[a] Burkhardt et al. (2014). [b] McDonough (2014). [c] Palme and O'Neill (2014). [d] Salters and Stracke (2004). [e] Rudnick and Gao (2014). [f] This study. [g] Bezard et al. (2016). [h] Greber et al. (2014).

chondritic composition if coupled with the removal of isotopically light lower crustal residue, either through crustal erosion in a subduction zone environment (e.g. Clift and Vannucchi, 2004; Willbold and Stracke, 2010) or by crustal delamination (e.g. Kay and Kay, 1993; Lustrino, 2005). Thus more analyses of Mo concentration and $\delta^{98/95}$Mo from a wider range of continental crustal samples of different age and depth would be valuable for assessing this hypothesis.

5.5. The late-Archean mantle

There is on-going debate about the nature of continental crust growth over time, but many models suggest a systematic increase in continental mass and change in mechanism of continent formation through time. In this light – and the discussion above – it might be expected that the Mo isotopic composition of the depleted mantle would decrease through time with net growth of isotopically heavy continents. This consideration makes it interesting to attempt to constrain the composition of the Archean mantle, which is perhaps best tackled using komatiites. These rocks are assumed to have formed by high-degree partial melting of the mantle at high temperatures (e.g. Arndt, 1977; Nisbett et al., 1993; Puchtel et al., 1996; Puchtel et al., 1997; Puchtel et al., 2004a; Puchtel et al., 2004b; Connolly et al., 2011), which most likely minimised any potential isotope fractionation during melting (Greber et al., 2015).

Greber et al. (2015) analysed the Mo isotope composition of series of well-characterised late-Archean komatiite suites, including samples from the Weltevreden Formation (Barberton Greenstone Belt, South Africa), Pyke Hill (Abitibi Greenstone Belt, Canda) and the Vicoria's Lava Lake Formation (Vetreny Belt, Fennoscandia). The overall range in $\delta^{98/95}$Mo varies considerably between −0.32 and +0.07‰ (Fig. 8). Samples from the Victoria's Lava Lake formation, for which independent evidence points towards potential assimilation of pre-existing crust, are off-set towards heavier, crustal isotopic composition. This highlights the effect of secondary processes potentially affecting the $\delta^{98/95}$Mo composition of the primitive komatiitic lavas and – in turn – constraining the Mo isotope composition of the Archean mantle. After further excluding altered samples, Greber et al. (2015) suggested a late-Archean mantle $\delta^{98/95}$Mo value of −0.21 ± 0.06‰ (2SE) based on the weighted average of the least altered komatiite formations, which is within uncertainty indistinguishable from the modern depleted mantle value inferred from Bezard et al. (2016). At face value, this consistency in $\delta^{98/95}$Mo for the convecting mantle over geological time may indicate the majority of continental material may have formed during Archean times, a view that is supported by independent constraints based on Hf model ages in crustal zircons (e.g. Dhuime et al., 2012). This has important bearings on the use of Mo isotopes to trace recycled components as addressed below. Yet, it should be noted, that very few komatiites suites are truly unperturbed by secondary processes such as crustal contamination (e.g. Arndt and Jenner, 1986) or, even more severely for the Mo isotope system, hydrothermal alteration (see above).

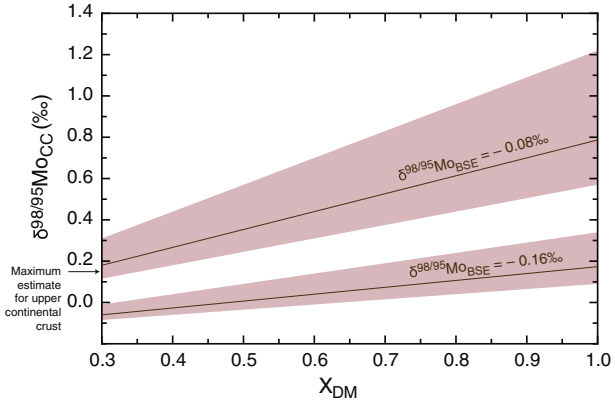

Fig. 7. Modelled Mo isotope composition of the continental crust (CC) as a function of size of the depleted mantle (X_{DM}; relative to the mantle) and the Mo isotopic composition of the bulk-silicate Earth. The two models assume a bulk silicate Earth with $\delta^{98/95}$Mo identical to that of chondritic meteorites (−0.16‰, Burkhardt et al., 2014) or $\delta^{98/95}$Mo = −0.08‰, i.e. a core-depleted mantle that has been augmented by addition of a late veneer component (see text). All other values used in the calculations are given in Table 1. Upper and lower bounds for each model represent continental crust – depleted mantle distribution coefficient of 20 and 40 (see text). Maximum estimate for upper continental crust from Greber et al. (2014).

6. Mass dependent Mo isotope variations as tracers of recycled crustal components in the mantle?

Key findings of current studies on the Mo isotope composition of igneous rocks so far include that (1) the oceanic lithosphere recycled into the mantle at destructive plate margins has a Mo isotope composition most likely lighter than that of unaltered oceanic crust (Freymuth et al., 2015); that (2) the mantle has a slightly sub-chondritic $\delta^{98/95}$Mo composition of ca. −0.21‰ potentially since the late Archean (Freymuth et al., 2015; Greber et al., 2015; Bezard et al., 2016); and that (3) the continental crust has a super-chondritic $\delta^{98/95}$Mo composition with a tentative upper limit for the upper continental crust of ca. +0.15‰ (Greber et al., 2014; Voegelin et al., 2014). It can be assumed that the oceanic crust has the same Mo isotope composition as the mantle from which it was derived from (Bezard et al., 2016), but is then subsequently perturbed towards a lighter composition during the subduction zone processing and before recycling into the mantle (Freymuth et al., 2015). This offers the opportunity to use Mo isotope

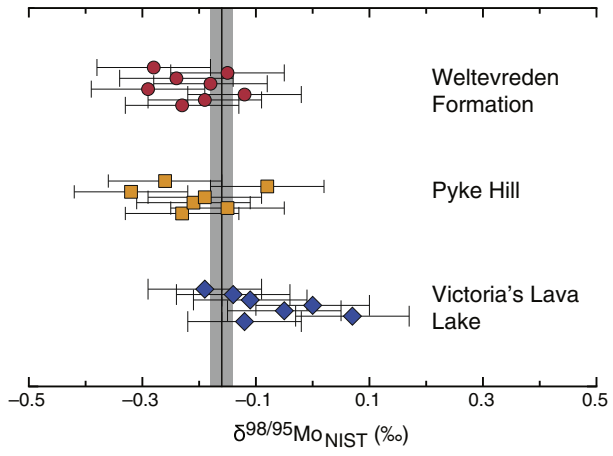

Fig. 8. Mass-dependent Mo isotope variations ($\delta^{98/95}$Mo) for least contaminated late-Archean komatiite suites. Data taken from Greber et al. (2015). Also shown is the chondritic value from Burkhardt et al. (2014) for reference.

data to trace recycled crustal components in the mantle source of oceanic basalts. The isotopically heavy Mo signature for the (upper) continental crust (Greber et al., 2014; Voegelin et al., 2014) may manifest itself as a contrasting isotopically heavy component if subducted in the form of clastic sediments (i.e. continentally derived). Yet, ocean sediment covers outboard of subduction zones are very rarely dominated by purely clastic, 'terrigenous' material (Plank and Langmuir, 1998) and the Mo isotope composition of commonly subducted oceanic sediments analysed to date are isotopically light (Freymuth et al., 2015). While we do not exclude that upper crustal material may represent a recycled component in ocean island basalt sources (Weaver, 1991a; Weaver, 1991b; Chauvel et al., 1992; Eisele et al., 2002; Stracke et al., 2003a; Willbold and Stracke, 2006; Chauvel et al., 2008; Willbold and Stracke, 2010) we simply stress that the Mo isotope system remains insensitive to this type of input material (i.e. depositional processes, such as coating by Mo-rich and isotopically light Fe-Mn oxy-hydroxides dominate the Mo isotope budget of the sedimentary material). Although direct evidence for $\delta^{98/95}$Mo lighter than the depleted mantle still need to be confirmed in ocean island basalts (Willbold et al., 2012), mass-dependent molybdenum isotope variations in oceanic basalts thus hold a great potential as a new tracer for mantle recycling processes.

Our discussion of recycling Mo is from a modern day perspective, but it is clear that the surface cycle of Mo has changed dramatically over Earth history with varying abundance of oxygen in of the atmosphere and oceans (e.g. Lyons et al., 2014). Indeed, such changes are a major consideration in understanding the geodynamic cycle of U (Andersen et al., 2015). Evolution of surface redox will influence the Mo isotopic inputs to the subduction system – in a reduced ocean the production of isotopically light sediments by surface absorption and isotopically heavy components from interaction with residual seawater will not occur. Thus the picture outlined above will change further back in Earth history. However, we have argued that the dominant process leading to an isotopically heavy Mo flux to the continents and a complementary light, deep recycled component is fractionation during dehydration of the subducting slab (Freymuth et al., 2015). Although the redox state of the release fluids may change, Mo^{6+} remains the dominant species even at mantle oxygen fugacities, so its fluid mobility and behaviour in this environment seems unlikely to change.

7. Summary and conclusions

With the data available, a broad picture of the Mo isotope systematics in magmatic systems seems to emerge. We can therefore draw up a rough conceptual framework for future studies as well as formulate some working hypotheses that could be tested using future larger databases and dedicated studies.

Differentiation appears to have a limited effect on Mo isotope data in magmatic rocks. Differences in bonding environments of Mo between melts and minerals should result in isotopically lighter solid phases, as has been shown for mica, hornblende and molybdenite. The overall incompatibility of Mo during differentiation, however, means that such fractionations are not clearly manifest in the evolving magmas.

The most characteristic Mo isotope signature in silicate rocks is related to the chemical and physical processes operating in subduction zone environments. Several lines of evidence suggest that dehydration processes within the subducting plate lead to a net flux of isotopically heavy Mo into the arc, again as a result of a preference for the lighter isotopes for the solid phases. Low $\delta^{98/95}$Mo values have also been reported for some arc-related mafic rocks, which may be a consequence of sediment addition although this process still needs to be clearly demonstrated in unaltered samples. Current data and models suggest that the overall loss of isotopically heavy Mo into the arc system leads to a residual plate with an isotopically light composition. Assuming that the continental crust formed as an arc crust, this further implies an isotopically heavy bulk continental crust, which is hinted at in existing data but needs to be substantiated. Although this seems to be a good working model, it can only be confirmed by further studies of magmatic arc systems. 'Simple' island arc systems, like the Mariana arc, are essential in establishing an initial framework that can then serve as a reference for more complex arc systems, such as juvenile and mature continental arcs (like the Andes) or arcs that involve more complex scenarios (i.e. the Mediterranean). In addition, experimental studies aiming to quantify the extent of isotope fractionation associated to fluid equilibration with titanifereous oxide phases are essential in testing the above model.

Molybdenum isotope data for inner solar system objects, such as the majority of chondritic as well as iron meteorites reveal are remarkably uniform $\delta^{98/95}$Mo composition. While it is likely that core formation occurred at temperatures high enough to have induced only minor fractionation between metallic core and silicate mantle, the subsequent extraction of continental crust from the mantle seems to have resulted in more significant differences, potentially related to the subduction process described above. Initial data suggest a slightly sub-chondritic $\delta^{98/95}$Mo for the modern depleted mantle and a complementary super-chondritic $\delta^{98/95}$Mo for the upper continental crust. Qualitative mass balance calculations suggest a value between ca. +0.10 and 0.35‰ for the $\delta^{98/95}$Mo of the bulk continental crust, assuming a chondritic bulk silicate Earth composition and that extraction of the continental crust resulted in whole-sale depletion of the mantle. One working estimate suggests a maximum value of $\delta^{98/95}\text{Mo} = +0.15$ for the upper continental crust. To date, no data are available for the lower continental crust and only a handful of data exists for mid-ocean ridge basalts. Clearly, refining this potential mass-balance by a better quantification of the Mo isotope composition of the crust and the mantle is of considerable interest.

Data from komatiites suggest a $\delta^{98/95}$Mo for the Archean convecting mantle similar to the modern mantle (ca. −0.21‰), which may imply early extraction of an isotopically heavy continental crust, but this important observation needs confirmation. Current subduction appears to be fluxing isotopically light Mo into the mantle, and this has considerable promise new tracer of crustal recycling.

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